Methylation of the oligomers was performed by Hakomori's method [8].

The hydrolysis of the methylated products was carried out by their successive treatment with formic and sulfuric acids [7]. The hydrolysates were studied by PC (system 5, revealing agent 1). Part of each of the hydrolysates was reduced with sodium tetrahydroborate, acetylated, and studied by GLC.

SUMMARY

The primary structures of the arabinoglucuronoxylans of the stems of common buckwheat and of *Polygonum weyrichii* have been established. It has been shown that the polysaccharides differ by their degree of branching and also by the nature of the attachment of some of the side chains.

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PHOSPHOLIPIDS OF THE GRAPE

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In the berries of the cultivated grape vine *Vitis vinifera* L. nine phospholipid fractions have been identified, the main ones being phosphatidylcholines and phosphatidylethanolamines. The composition and position distribution of the fatty acids has been studied.

The influence of phospholipids (PLs) on the properties of the products of the processing of grapes and, in particular, on the stability [1], the organoleptic properties [2], and the direction of redox processes in wines [3] is a matter of doubt at the present time. Nevertheless, the PLs of the grape have scarcely been studied in the chemical respect [4].

The present paper gives the results of an investigation of the chemical composition and structural features of the PLs of the grape and its component parts (flesh, skin, seeds).

The extraction and purification of the lipids was carried out from the component parts and whole fruit of the cultivated grapevine *Vitis vinifera* L., of the Pinot Gris variety by a modified Bligh–Dyer method [5], and the PLs were isolated by column chromatography on silica gel and were subfractionated by two-dimensional TLC in systems 1 (first direction) and 2 (second direction) [6].

According to the experimental results, the amounts of PLs in the total lipids was small, amounting to 9.7% for the seeds, 6.6% for the flesh, and 2.3% for the skins.

Nine phosphorus-containing spots were detected with the following R_f values (in the second direction): 0.75 (diphosphatidylglycerols — DPGs); 0.61 (phosphatidic acids — PAs); 0.57 (phosphatidylethanolamines — PEs); 0.44 (phosphatidylglycerols — PGs); 0.31 (phosphatidyl-

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cholines — PCs); 0.26 (phosphatidylserines — PSs); 0.13 (phosphatidylinositols — PIs); 0.10 (lysophosphatidylethanolamines — LPEs); and 0.05 (lysophosphatidylcholines — LPCs).

Preliminary identification of the PLs was carried out by treating the chromatograms with specific reagents to reveal phosphorus-containing lipids (Dittmer—Lester reagent in the Vas'kovskii—Kostetskii modification), aminophospholipids (ninhydrin), choline-containing PLs (Dragendorff reagent) [6]. The IR spectra of homogeneous fractions of the PLs corresponded to those given in the literature [7, 8].

The structures of the individual PLs were confirmed with the aid of severe acid hydrolysis [7]. Free FAs and glycerol were detected in the hydrolysates of all the PLs. The hydrolysates of the individual fractions of the PLs were shown to contain choline (PCs, LPCs), monoethanolamine (PEs, PLEs), inositol (PIs), and serine (PSs).

Chromatographic separation, chemical analysis, the quantitative determination of water- and fat-soluble components of the molecules, and also the determination of the molar ratios between the main fragments of the PLs permitted all the fractions detected to be reliably identified.

Below we give the compositions and amounts of the PL fractions of the grape and its component parts (%):

Object	LPCs	LPEs	PIs	PSs	PCs	PGs	PEs	PAs	PPGs	Total amount of PLs, mg/kg
Flesh	2,7	3.4	4,0	7,6	31,2	12,3	27,4	2,2	9,2	118,8
Skin	3,2	4,0	6,1	8,8	27,6	10,4	34,0	3,5	2,4	378,6
Seeds	1,9	2,2	8,1	10,4	25,1	6,3	36,3	6,7	3.0	11231,5
Berries	2,2	3,0	5,6	8,4	29,7	10,9	32,3	3,6	4,3	578,3

The structural elements of the grape form the following sequence in order of decreasing total PL content: seeds, skin, flesh. The sets of PL fractions in the grape and its structural elements are the same. Although the amounts of PLs in the grape and its component parts are quantitatively different, the group distributions are similar, on the whole. The PCs and PEs predominate, together making up more than 50% of the total PLs.

The fatty acids of the total PLs and the individual fractions were analyzed by GLC.

The position distribution of the FAs in the glyceride part of the PL molecules was determined by enzymatic hydrolysis with the aid of phosphatide acylhydrolase EC 3.1.1.4 (Table 1).

The PLs of the seeds were distinguished by the largest amount of unsaturated FAs, and the skin by the smallest amount. The amount of unsaturated FAs in the PLs of the flesh was twice as much as in the skin but considerably less than in the seeds. On the whole, the total PLs of the grapes and also the individual groups were characterized by high amounts of saturated FAs (more than 60%). The PLs of the grape were characterized by a high specificity of the distribution of the FAs: The degree of unsaturation of position 2 was 2-4 times greater than of position 1, which is a distinguishing feature of natural PLs [9].

In the determination of the possible compositions of the PLs, we based ourselves on the experimental results concerning the position distribution of the fatty acid radicals in their molecules and a mathematical method [9]. The number of molecular species calculated for the PCs was 114, and for the PEs 118, for the PIs 95, for the PSs 110, for the PGs 92, and for the PAs 135. Components the amounts of which were less than 1% were not taken into consideration. The majority of the molecular species of the PLs investigated were formed from long-chain acids and were present in amounts of less than 1%. The dominating species in all cases were formed by a combination of the 16:0, 18:0, 18:1, and 24:0 acids. On separately summing the amounts of the various types of PLs, the following group composition of the diglycerides was obtained:

Species	PCs	PEs	PIs	PSs	PGs	PAs
Disaturated	32,4	43,5	49,9	42.4	42,4	36,9
Diunsaturated	12,2	8,7	5,9	7,6	6,4	10.1
Saturated-unsaturated	46,9	37.8	36,0	42,4	45,3	44,6
Unsaturated-saturated	8,5	10,0	8,2	7.6	5,9	8,4

The group compositions of the PLs of the grape were basically similar. Disaturated and saturated-unsaturated PCs predominated (>80%). The high amount of these species in the total PLs of the grape makes them fairly stable to autooxidation, promoting the appearance of another property characterizing them — their antioxidant property — which has a considerable influence on the occurrence of redox processes in the products of the treatment of the grape [3].

TABLE 1. Composition and Position Distribution of the Fatty Acids in the Phospholipids of the Grape, %

Fraction	Fatty acid																			Sum	
	9:0	10:0	12:0	14:0	14:1	16:0	16:1	17:0	17:1	18:0	18:1	18:2	20:0	18:3	20:1	21:0	22:0	23:0	24:0	saturated	unsaturated
Flesh	0,4	0,7	3,2	5,6	0,3	24,0	2,7	1,1	0,3	20,8	19,5	3,7	1,3	2,5	0,1	0,7	2,6	0,4	10,1	70,9	29,1
Skin	2,0	0,3	1,7	2,6	—	18,1	0,6	0,9	—	22,1	8,4	3,0	5,9	1,8	—	4,4	2,9	4,0	21,3	86,2	13,8
Seeds	—	—	1,2	2,0	1,8	10,0	7,3	—	3,4	5,9	8,1	44,9	0,4	8,0	0,6	0,1	0,2	1,4	4,7	25,9	74,1
Sum																					
FLs of the grape	1,1	0,4	1,9	3,2	0,6	19,7	3,9	0,5	0,4	18,6	21,6	4,2	0,9	3,9	0,1	0,4	1,7	3,0	13,9	65,3	34,7
LPCs	0,5	—	1,1	4,7	1,9	20,5	4,7	0,2	1,3	13,1	20,5	5,6	0,4	2,3	0,6	0,1	0,6	1,7	20,2	63,1	36,9
LPES	1,9	0,1	2,7	3,6	0,2	15,8	2,5	1,1	0,7	16,7	20,7	3,6	0,1	2,7	—	0,9	0,8	4,3	21,6	69,6	30,4
PIs	1,4	0,7	0,9	2,3	0,9	24,0	4,9	0,1	0,1	25,8	19,9	2,0	1,7	1,6	0,3	—	2,2	1,3	9,9	70,3	29,7
Total																					
Position 1	2,3	0,9	2,1	3,1	0,7	28,3	1,7	0,1	—	30,4	10,6	0,8	2,2	0,2	0,1	—	3,4	2,0	11,1	85,9	14,1
Position 2	0,6	0,4	—	1,7	1,3	21,7	8,1	—	0,1	22,1	27,6	1,3	1,5	3,3	0,2	—	1,2	0,4	8,4	58,1	41,9
PSs	0,3	—	2,2	1,7	1,5	17,9	2,1	0,4	—	19,2	18,0	4,5	1,9	4,7	—	1,1	2,5	3,6	18,4	69,2	30,8
Total																					
Position 1	0,3	—	3,5	2,6	0,3	19,1	0,6	0,3	—	23,4	9,4	3,1	2,4	1,7	—	2,0	2,4	4,2	23,7	84,9	15,1
Position 2	—	—	1,1	0,8	2,8	14,9	3,7	0,2	—	14,1	29,0	6,4	1,5	8,1	—	0,4	1,9	3,1	12,0	50,0	50,0
PCs	1,3	0,6	1,7	3,5	0,7	18,4	4,5	0,7	0,6	14,3	23,0	5,3	0,5	4,9	0,2	0,1	0,9	2,4	16,4	60,8	39,2
Total																					
Position 1	2,0	0,9	2,5	4,8	0,2	24,5	2,6	1,0	0,2	20,5	11,4	3,1	0,3	3,1	0,1	0,1	0,6	2,0	20,1	79,3	20,7
Position 2	0,9	0,2	1,1	1,3	1,1	14,3	6,2	0,5	0,9	7,3	34,2	8,8	0,3	7,7	0,2	—	0,1	0,6	14,3	40,9	59,1
PGs	0,7	—	1,5	1,9	0,2	22,4	1,1	0,4	0,2	21,0	23,3	5,3	1,2	4,7	0,7	0,6	1,3	2,0	11,5	64,5	35,5
Total																					
Position 1	0,5	—	2,3	3,0	0,2	29,8	0,5	0,3	—	29,8	8,4	1,4	2,0	1,6	0,2	0,9	2,0	3,1	14,0	87,7	12,3
Position 2	0,3	—	0,9	0,7	0,3	19,7	0,7	0,2	0,2	15,1	34,2	8,1	0,4	7,6	0,6	0,4	0,9	1,0	8,7	48,3	51,7
PEs	1,5	0,3	2,4	3,0	0,3	21,3	5,1	0,5	0,3	23,4	19,7	4,2	1,3	2,1	—	1,7	2,4	3,3	7,2	68,3	31,7
Total																					
Position 1	1,9	0,4	3,1	3,7	0,2	23,1	2,0	0,6	0,2	28,1	13,9	1,1	2,0	1,3	—	2,2	4,0	3,9	8,3	81,3	18,7
Position 2	1,4	0,3	1,5	1,5	0,5	18,0	6,7	0,5	0,4	19,4	29,4	6,5	0,4	3,0	—	1,5	0,6	2,7	5,7	53,5	46,5
PAs	0,2	—	3,9	4,7	0,1	16,4	8,9	0,3	1,7	15,2	18,4	4,1	0,1	2,0	0,9	0,5	2,8	5,1	14,7	63,9	36,1
Total																					
Position 1	0,3	-	5,1	5,3	—	20,1	2,4	0,2	0,4	19,6	11,1	1,5	0,2	2,9	0,2	0,8	3,6	6,9	19,4	81,5	18,5
Position 2	0,2	—	2,9	3,0	0,2	12,9	16,5	0,2	2,8	12,1	25,1	7,0	—	1,2	1,9	0,3	2,7	2,9	8,1	45,3	54,7
DPGs	0,9	—	1,4	1,5	0,9	17,3	5,0	0,9	2,0	13,2	23,9	4,7	0,4	4,2	0,4	—	1,0	2,2	20,1	58,9	41,1

EXPERIMENTAL

As adsorbent for chromatographic analysis we used Woelm silica gel with particle dimensions corresponding to 100-150 mesh for columns and 150-200 mesh for thin layers. Chromatography was performed in the following solvent systems: 1) chloroform—methanol—7 N ammonia (65:30:4); 2) chloroform—methanol—acetic acid—water (170:25:25:6). The chemical and enzymatic hydrolyses of the PLs were carried out as described by Kates [7]. Phosphorus was determined by a spectrophotometric method [10]. The FAs liberated as the result of hydrolysis were separated from the lyso-PLs by TLC in the heptane—methyl ethyl ketone—acetic acid (42:7:5:0.5) system.

The mixture of FA methyl esters was separated on a Chrom chromatograph using a 2500 × 4 mm column with the solid support Celite 545 (60-80 mesh) and the liquid phase PEGS (18%); the column temperature was 197°C and the rate of flow of carrier gas (helium) 1.2 ml/min. The water-soluble products obtained after severe acid hydrolysis of the PLs (2 N HCl, 125°C, 48 h) [7] were identified by ascending paper chromatography. Choline, serine, and ethanolamine were identified in the phenol—ethanol—acetic acid (50:5:6) system and glycerol and inositol in the pyridine—ethyl acetate—water (2:5:5) system. The quantitative determination of the nitrogen-containing products of the hydrolysis of the PLs and the glycerol was performed as described by Kates [7].

SUMMARY

It has been found that the main components of the total phospholipids of the grape and its component parts are phosphatidylcholines and phosphatidylethanolamines, which make up more than 50% of the total phospholipids. Seven minor components have been isolated and characterized: lysophosphatidylcholines, lysophosphatidylethanolamines, phosphatidylinositols, phosphatidylserines, phosphatidylglycerols, phosphatidic acids, and phosphatidylglycerols. The glycerophospholipid structures of the main and minor components of the phospholipids have been established on the basis of the results of acid hydrolysis. The position **distributions** of the fatty acids in the molecules of the phospholipids have been determined with the aid of enzymatic hydrolysis by phospholipase A_2 and their possible molecular compositions have been calculated. A predominance of disaturated and saturated-unsaturated species of phospholipids has been found. **Differences have been** revealed in the amounts and fatty-acid compositions of the phospholipids of the flesh, skin, and seeds.

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